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Impact of electron–electron cusp on configuration interaction energies

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The effect of the electron–electron cusp on the convergence of configuration interaction (CI) wave functions is examined. By analogy with the pseudopotential approach for electron–ion interactions, an effective electron–electron interaction is developed which closely reproduces the scattering of the Coulomb interaction but is smooth and finite at zero electron–electron separation. The exact many-electron wave function for this smooth effective interaction has no cusp at zero electron–electron separation. We perform CI and quantum Monte Carlo calculations for He and Be atoms, both with the Coulomb electron–electron interaction and with the smooth effective electron–electron interaction. We find that convergence of the CI expansion of the wave function for the smooth electron–electron interaction is not significantly improved compared with that for the divergent Coulomb interaction for energy differences on the order of 1 mHartree. This shows that, contrary to popular belief, description of the electron–electron cusp is not a limiting factor, to within chemical accuracy, for CI calculations. © 2001 American Institute of Physics.
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I. INTRODUCTION

The primary difficulty in solving the Schrödinger equation for many-electron systems arises from the presence of the electron–electron interaction, which results in a problem nonseparable in the electron coordinates. Configuration interaction (CI) calculations use an expansion of the many-body wave function in configuration state functions (CSF) given by spin coupled sums of determinants built from single-particle orbitals. **One of the central difficulties for the convergence of the CI expansion is thought to arise from the behavior of the Coulomb interaction at small electron–electron separations.^{1–10} The many-body wave function must have an appropriate cusp at electron coalescences so that the infinite Coulomb interaction term is exactly cancelled by an opposite divergence of the kinetic energy.¹¹**

It is often stated in the literature that failure of the CI expansion to reproduce the correct electron cusp, i.e., the short-range part of the Coulomb hole, leads to a slow convergence in the energy with respect to the number of CSF's.³ While this has been shown^{2,5} in the asymptotic regime (i.e., very large angular momentum l and energy errors of the order of 10^{-6} Hartree), it is not clear that it applies in the practical regime (mHartree accuracy) for multielectron systems.

Explicit inclusion of terms in the interelectronic distance

(r_{12} methods)^{4,12} or the use of correlated (geminal) Gaussian basis functions¹³ significantly improve the convergence of a CI calculation. For the helium atom, the inclusion of r_{12} terms⁵ yields an expansion in partial waves converging asymptotically as l^{-6} or better, instead of a slow l^{-3} , where l is the maximum angular momentum in the expansion. Baker *et al.*¹⁴ also showed that using basis functions with the same analytic structure as the true wave function (depending on powers and logarithms of r_{12}) leads to a reduced expansion length. The success of methods explicitly including r_{12} terms has been attributed to their correct description of the short-range part of the interaction.

A completely different point of view, taken by Gilbert in 1963,¹⁵ is that the difficulty of CI wave functions in describing short-range effects of the cusp are energetically unimportant and that the benefit of the explicitly correlated approach is that the *entire* Coulomb hole, with a size on the order of the atomic orbitals, is much easier to describe in terms of interelectronic coordinates. Gilbert's suggestion appears to have received little attention and the idea that smoothing out the Coulomb potential and *removing the cusp altogether* will automatically lead to an improved CI convergence has been stated in the literature.^{9,16} However, no systematic studies of the effect of the electron cusp on CI energy convergence at the level of interest for chemical accuracy (1 mHartree for total energies) have been presented.

In this paper, we explore whether a significant improve-

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ment in the convergence of the CI expansion is obtained when the true Hamiltonian is replaced by one which has a smooth and finite electron–electron interaction (pseudo-interaction) at short distances and, consequently, smooth eigenfunctions with no cusps.

Surprisingly, in calculations for the He and Be atoms, we find that removing the divergence of the Coulomb potential at electron–electron coalescences does not significantly reduce the length of the CI expansion, thereby substantiating the argument put forward by Gilbert¹⁵ that the slow convergence should be attributed to difficulties in describing, not the interelectron cusp, but the intermediate-range electronic correlation. The poor treatment of the interelectron cusp in the CI expansion is not a limiting factor at the mHartree level of accuracy on the total energy. To further confirm this result, we calculate the energy within quantum Monte Carlo (QMC) for the true electron–electron interaction with accurate wave functions which explicitly contain interelectronic coordinates, and then deliberately remove the short-range correlation term related to the cusp, keeping other parts of the wave function unchanged. We find that the removal of the cusp has a very small effect on the variational energy. Finally, we demonstrate that the convergence behavior of the CI expansion as a function of angular momentum in the range practical for many applications ($l < 6$) is largely unaffected by the smoothing of the electron cusps. Therefore, the angular momentum convergence numerically observed by other authors⁷ is related to problems associated with intermediate range correlations, not the cusp region as such.

In Sec. II, we describe the pseudopotential used for the electron–electron interaction and briefly present the QMC and CI methods. In Sec. III, we report the QMC and CI energies for He and Be atoms using the true and pseudo electron interaction. In Appendices A and B, we discuss the numerical generation and accuracy of the electron pseudo-interaction, and in Appendix C we define a short-range correlation term which can be associated with it. In Appendix D, we briefly discuss the evaluation of two-electron integrals for the pseudo-interaction.

II. COMPUTATIONAL METHODS

A. Electron–electron pseudo-interaction

When modifying the short-distance electron–electron interaction, we wish to keep the intermediate- and long-range correlation properties of the many-body eigenstates unchanged. This will allow us to isolate systematically the effects of the short-range cusp-like behavior in the wave function. To achieve this, our new (smooth) interaction should ideally have electron–electron scattering properties identical to the true interaction for all energies. If this were the case, all many-electron eigenvalues would be identical for both interactions. While this ideal cannot be exactly realized, we expect that a potential with the same scattering properties as the true interaction over a sufficiently wide range of scattering energies will give many-electron eigenvalues very close to the true ones.

This goal for electron–electron scattering is analogous to the problem of electron–ion scattering addressed in the well-

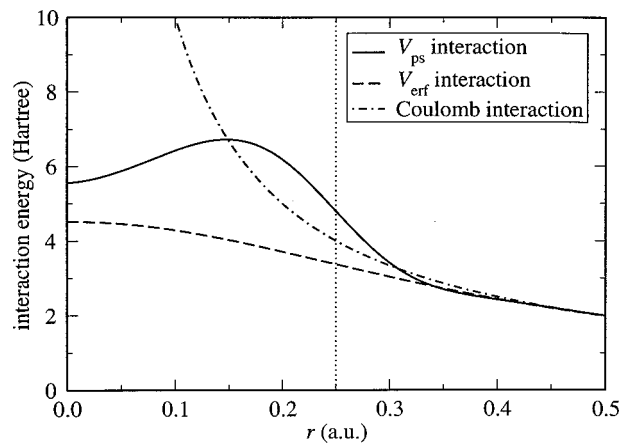


FIG. 1. Norm-conserving electron pseudo-interaction (solid line) and smooth interaction V_{eff} (dashed line), each with a cut-off radius $r_c = 0.25$ a.u. (indicated by a vertical dotted line), and the true $1/r$ interaction (dash-dot line), as functions of the electron separation r .

established pseudopotential method.¹⁷ In that approach, the aim is to produce a smooth electron–ion potential which reproduces the single-particle eigenvalues of the true system over a range of energies, and has the same single-particle wave functions outside some suitably chosen cut-off radius r_c . Such pseudopotentials are generated for the isolated atom but may then be used with a high level of accuracy in molecules and solids. In solids, the smoothness of the potential greatly improves the convergence of plane-wave expansions for single-particle orbitals.¹⁸

Following the success of norm-conserving pseudopotential methods in the context of the electron–ion scattering problem, we generate a norm-conserving pseudo-interaction for the two-electron scattering problem, which will replace the true e^2/r electron–electron interaction inside a cut-off radius r_c . Since the electron–electron interaction is repulsive and has no bound states for an isolated pair of electrons, we use, with some minor modifications, the generalized norm-conserving method devised by Hamann¹⁹ to generate pseudopotentials for electron–ion interactions at unbound, scattering state energies. The numerical details of this approach are presented in Appendix A.

In Fig. 1, we show a pseudo-interaction potential V_{ps} generated by this approach, along with the true e^2/r interaction and a smooth but not norm-conserving interaction, $V_{\text{eff}}(r) = e^2 \text{erf}(r/r_c)/r$, as used by Savin and co-workers²⁰ in a different context. In Appendix B, the accuracy of such scattering potentials in reproducing the exact eigenstate energies is analyzed qualitatively using first-order perturbation theory. In Appendix C, we define a short-range interelectronic correlation term, which can be directly related to the replacement of the divergent Coulomb interaction with a smooth norm-conserving interaction.

B. Quantum Monte Carlo calculations

We employ QMC methods to determine accurate energies both for the Coulomb and the pseudo-interaction. The wave functions Ψ used in QMC are of the form given in Ref. 21 and explicitly depend on the interelectronic coordinates.

They include parameterized terms to describe electron–nucleus, electron–electron, and electron–electron–nucleus correlation, as follows:

$$\Psi = \left(\sum_n d_n D_n^\uparrow D_n^\downarrow \right) J(r_i, r_j, r_{ij}). \quad (1)$$

D_n^\uparrow and D_n^\downarrow are the Slater determinants of single particle orbitals for the spin-up and down electrons, respectively, and J is a Jastrow factor of the form

$$J(r_i, r_j, r_{ij}) = \prod_i \exp(A_i) \prod_{ij} \exp(B_{ij}) \prod_{ij} \exp(P_{ij}), \quad (2)$$

where A is an electron–nuclear term (which could be omitted if a sufficiently large single particle basis were used in constructing the determinantal part), B is an electron–electron term incorporating the cusp at small r_{ij} , and P is a smooth function of the electron coordinates, r_i and r_j , as discussed in detail in Ref. 21. For the pseudo-interaction calculations, the B term is omitted. The parameters in the determinant and Jastrow factor are optimized within QMC using the variance minimization method²² and the accuracy is tested at the variational level. The wave function is then used in diffusion Monte Carlo (DMC), which produces the best energy within the fixed-node approximation (i.e., the lowest-energy state with the same nodes as the trial wave function).

For a given interaction, this method yields the exact eigenvalue (within statistical sampling noise) for the ground state of the He isoelectronic series since the singlet ground-state wave function of a two-electron system is nodeless. For He, only one determinant is used in the wave function. For the Be atom, the $2s$ and $2p$ configurations are included in the determinantal part of the wave function and DMC gives the best energy subject to the fixed-node condition. To isolate the effect of the pseudo-interaction from the fixed-node approximation, we keep the nodal structure of the wave function fixed while modifying the electron–electron interaction.

C. Configuration interaction calculations

The CI calculations are performed using the Monte Carlo configuration interaction (MCCI) method.^{23,24} In a MCCI calculation, a coefficient threshold c_{\min} is defined, configurations are randomly generated, and, after a variational calculation, coefficients of magnitude below c_{\min} are rejected. This procedure is repeated until a desired degree of convergence in the CI calculation is achieved. A full CI (FCI) calculation can be obtained for $c_{\min}=0$. The fact that the MCCI procedure does not rely on a pre-selection of CSF's makes it well-suited for our study: The dynamical selection of configurations allows for rejection of CSF's which may no longer be needed with the smooth electron interaction.

For use in the CI approach, the pseudo-interaction V_{ps} is represented (in Hartree atomic units) as a sum of the smooth function V_{erf} plus n_G Gaussian terms, as follows:

$$V_{\text{ps}}(r) = \frac{\text{erf}(r/r_c)}{r} + \sum_{i=1}^{n_G} c_i \exp(-d_i r^2). \quad (3)$$

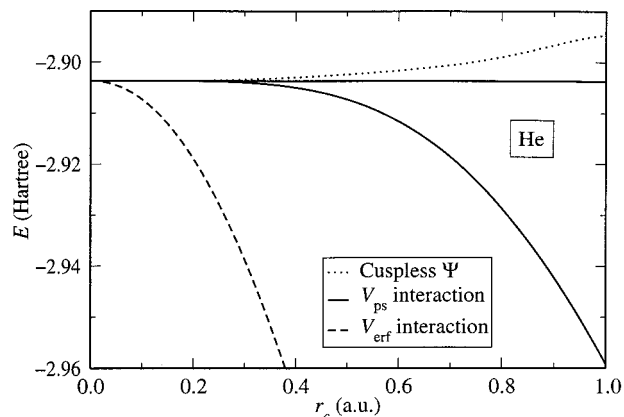


FIG. 2. He atom ground-state energy E as a function of cut-off radius r_c , obtained from DMC calculations using various forms of the electron–electron interaction: (a) the norm-conserving pseudo-interaction V_{ps} (solid line); (b) the smooth interaction V_{erf} (dashed line). The curves are polynomial fits to the calculated DMC values, as discussed in the text. The horizontal line shows the exact value (Ref. 26) for the He ground state. Also shown are variational energies, with the true Coulomb interaction, upon removal of the electron cusp (see Appendix C) from the wave function used in the DMC calculations (dotted line).

This reproduces the $1/r$ tail of the Coulomb interaction and the smooth, finite form of the pseudo-interaction at short distances. The parameters c_i and d_i are found by least-squares fitting (for radii $r < 3r_c$) to the numerical potential, generated as described in Appendix A. For the CI results presented below, the potential was fitted using $n_G=9$. QMC calculations of the He atom energy with the numerical potential and with the fitted potential show a negligible difference (less than 0.02 mHartree for all values of $r_c < 1$ a.u.).

Evaluation of the pseudo-interaction $V_{\text{ps}}(r)$ can be implemented in codes for Gaussian integral calculation since it is possible to compute the two-body matrix elements both of $\exp(-dr^2)$ and $\text{erf}(r/r_c)/r$ in the CI basis. Matrix elements of the interaction $\text{erf}(r/r_c)/r$ for all s -type basis functions have already been given in Ref. 20. For both types of interaction, a simple modification to the integral codes is possible if the standard two-electron integrals are calculated using the method of Rys quadrature.²⁵ Details of two-body integral evaluation with the modified form of the electron interaction are given in Appendix D.

III. He AND Be ATOMIC ENERGIES WITH PSEUDO-INTERACTIONS

To test the impact of the interelectron cusp on the energy, we calculate the total energies of He and Be atoms, replacing the true $1/r$ electron interaction with the norm-conserving pseudo-interaction $V_{\text{ps}}(r)$, generated for various values of the cut-off radius r_c . For comparison, we also present results for the smooth but not norm-conserving potential $V_{\text{erf}}(r) = \text{erf}(r/r_c)/r$. The results in this section are obtained from QMC and CI calculations.

A. Ground state of the He atom

In Fig. 2, we show the singlet ground state energies of the He atom calculated with a norm-conserving electron–electron interaction V_{ps} generated as in Sec. II, for various

TABLE I. Calculated correlation energy for the He atom with a cc-pVQZ basis set, as a function of cut-off radius r_c and the CI coefficient threshold c_{\min} . The energy units are mHartree. The right-hand column (HF – QMC) shows the full correlation energy [i.e., the difference between the Hartree–Fock energy, calculated with this basis, and QMC (exact) energy]. The percentages indicated are the fractions of the full CI correlation energy for each value of r_c .

r_c (a.u.)	3×10^{-2}	2×10^{-2}	1×10^{-2}	c_{\min} 1×10^{-3}	1×10^{-4}	0.0	HF – QMC
0.95	2.15	15.10	12.98	18.72	18.96	18.96	19.56
	11.01%	77.21%	66.36%	95.69%	96.94%	96.95%	100.00%
0.80	6.09	18.45	16.93	25.11	25.16	25.16	25.76
	23.66%	71.64%	65.74%	97.48%	97.67%	97.67%	100.00%
0.50	8.64	27.23	32.79	36.32	36.32	36.32	37.18
	23.24%	73.24%	88.19%	97.69%	97.69%	97.69%	100.00%
0.20	14.07	28.93	35.27	40.75	40.75	40.75	41.93
	33.57%	69.00%	84.13%	97.20%	97.20%	97.20%	100.00%
0.10	9.37	28.98	35.35	40.89	40.89	40.89	42.18
	22.22%	68.71%	83.80%	96.94%	96.94%	96.94%	100.00%
0.00	27.44	30.61	36.09	40.90	40.90	40.90	42.21
	65.01%	72.52%	85.50%	96.90%	96.90%	96.90%	100.00%

values of the cut-off radius r_c . The values obtained from QMC (exact) calculations are shown. We also plot the energies calculated using the $V_{\text{erf}}(r)$ interaction. The horizontal line indicates the exact energy $E_0 = -2.903\,724$ Hartree for the true Coulomb interaction.²⁶

The calculated QMC energies for V_{ps} and V_{erf} in Fig. 2 are fitted with polynomial expansions of the form: $E(r_c) = E_0 + ar_c^2 + br_c^3 + cr_c^4 + dr_c^5 + er_c^6$. As discussed in Appendix B, any potential which differs from the exact $1/r$ interaction would be expected, from first-order perturbation theory, to converge at least quadratically in r_c to the exact energy E_0 for small r_c . Since V_{erf} is not explicitly constructed to eliminate first-order errors in $V_{\text{erf}}(r) - 1/r$, quadratic convergence is seen for V_{erf} and the fitting parameters are: $a = -0.3279$, $b = -0.3839$, $c = 0.6758$, $d = -0.2622$, and $e = 0$. On the other hand, the norm-conserving pseudo-interaction construction of Sec. II A explicitly ensures that the first-order perturbation correction to the energy is zero. The He ground-state energy as a function of r_c using V_{ps} can indeed be fitted without the quadratic term, and even the cubic term proves to be small, the polynomial coefficients being: $a = 0$, $b = 0.0188$, $c = -0.1023$, $d = 0$, and $e = 0.0280$. For He, the energies obtained using $V_{\text{ps}}(r)$ are within 1 mHartree of the energy computed with the true Coulomb interaction for values of $r_c < 0.4$ a.u. Since the typical electron–electron distance in the He ground state is of the order of 1 a.u., these results indicate that the first peak of the electron pair-distribution function provides a good measure of how large a cut-off radius r_c may be used to obtain accurate total energies with $V_{\text{ps}}(r)$: r_c should be approximately half the radius at which this first peak occurs. The same criterion for the largest allowed r_c value was found to hold for other systems (not shown), viz. the He triplet state, the He isoelectronic series, and multielectron atoms. In a qualitative way, this condition is similar to the criterion used in the generation of electron–ion pseudopotentials, where the cut-off radius is chosen to be inside the peak of the valence electron density.

Also shown in Fig. 2 are the variational energies (with the true Coulomb electron–electron interaction) obtained for

the He ground state by removing the electron cusps from the accurate trial wave function which was determined by variance minimization for use in the DMC calculations, as specified in Eq. (C1). This trial wave function includes considerable variational freedom in the interelectronic terms and obtains 100% of the correlation energy. As can be seen in Fig. 2, removal of the cusp out to radii of 0.5 a.u. causes little degradation of the quality of the energy obtained with this wave function. Thus the success of interelectronic terms in obtaining good variational energies is not primarily due to their description of the short-range cusp behavior.

This trend is further borne out when we look at the convergence of partial CI expansions within a given single-particle basis set for the MCCI method. The CI calculations were performed with the correlation consistent polarized valence double-zeta (cc-pVDZ), triple-zeta (cc-pVTZ), quadruple-zeta (cc-pVQZ), and quintuple-zeta (cc-pV5Z) basis sets of Dunning²⁷ with the electron interaction V_{ps} for various values of r_c . All four basis sets show similar behavior and we present only the cc-pVQZ results in detail. Table I shows the correlation energy obtained as a function of cut-off radius r_c for various values of the expansion coefficient threshold c_{\min} . The full CI result is obtained when $c_{\min} = 0.0$. For larger values of the cut-off radius r_c (upper rows of table), the total correlation energy is smaller, as the variation of the interaction V_{ps} becomes smaller around the typical separation distance of the electrons. However, the fraction of the correlation energy which is recovered at a given CI threshold level c_{\min} depends little on the value of r_c .

Figure 3 shows the number of CSF's in the CI expansion as a function of cut-off radius r_c for various values of the expansion coefficient threshold c_{\min} . For values of $c_{\min} > 3 \times 10^{-2}$, one is quickly reduced to a few CSF's and finally to the Hartree–Fock solution. As with the correlation energies, for a given threshold c_{\min} , the number of CSF's shows relatively little change for values of r_c between 0 and 0.95. Again, it is worth bearing in mind that the typical electron–electron separation is 1 a.u. and that a cut-off radius $r_c = 0.95$ represents a very smooth interaction. Thus, removal of electron cusps does not result in a significant reduction in

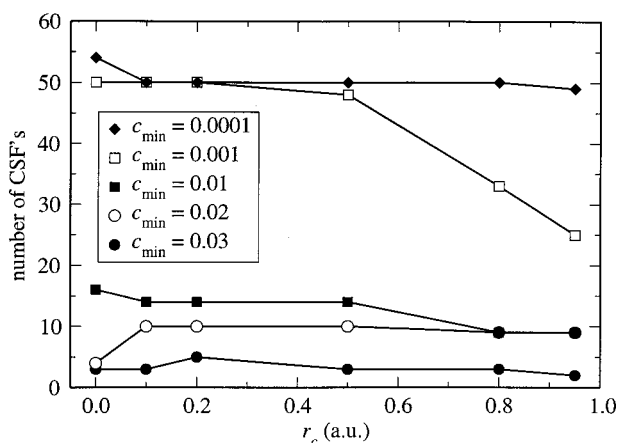


FIG. 3. The number of configuration state functions (CSF) in the CI expansion for the He atom with the cc-pVQZ basis set as a function of r_c . Results are presented for coefficient thresholds c_{\min} of 0.03, 0.02, 0.01, 0.001, and 0.0001.

the number of contributing configurations in the CI expansion.

We next demonstrate that removal of the electron cusp does not significantly change the convergence properties of CI expansions as the highest angular momentum quantum number is increased in the single particle basis sets. In Fig. 4, FCI energies for He are displayed against increasing basis set size in the correlation consistent series from Dunning, and hence increasing angular momentum number in the basis. The convergence in the FCI energy with increasing basis set size is compared for electron interaction V_{ps} , with values of the cut-off radius r_c from 0 to 0.8. Fitting these energies to a function similar to the asymptotic form derived in Ref. 2,

$$E = E_0 + \frac{a}{L^3} + \frac{b}{L^4}, \quad (4)$$

where L is the maximum angular momentum in the basis, gives best values of $a \approx 0.038$ and $b \approx -0.022$ for each value of $r_c \leq 0.2$ and gives $a \approx 0.02$ and $b \approx -0.01$ for $r_c \geq 0.5$. Thus, the predominant $1/L^3$ convergence of the energy is present for all values of r_c investigated here.

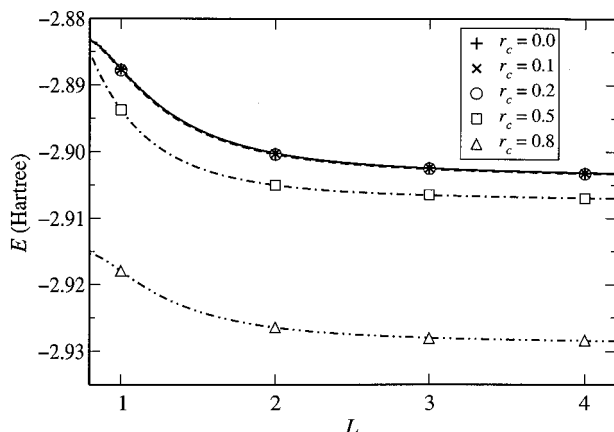


FIG. 4. Full CI energies E for the ground-state He atom as a function of L , the maximum angular momentum in the basis set used, calculated using the electron interaction V_{ps} with values of the cut-off radius r_c from 0 to 0.8.

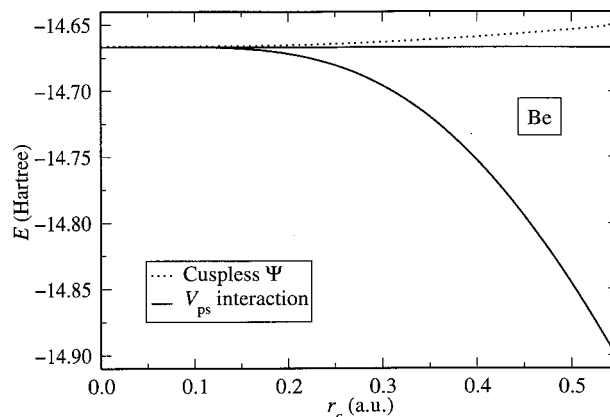


FIG. 5. Be atom ground-state energy E as a function of cut-off radius r_c , obtained from (a) DMC calculations using the norm-conserving pseudo-interaction V_{ps} (solid line); (b) variational calculations using the true Coulomb interaction upon removal of the electron cusp from the trial wave function (see Appendix C) used in the DMC calculation (dashed line).

Although the asymptotic form in Eq. (4) fits the results well, the parameters a and b do not have the asymptotic values, $a = 0.025$ and $b = 0.008$, found for the angular momentum convergence associated with the short-range cusp.³ Two factors cause this discrepancy: (i) not only higher angular momentum functions are added as L is increased in the Dunning basis sets; (ii) more importantly, we are not near the asymptotic regime, where expansion of the short-range cusp would be the dominant energy correction.

B. Ground state of the Be atom

The qualitative nature of the CI energy convergence seen in the previous section is not special to the He atom. Figure 5 shows the DMC calculated ground-state energies of Be for various cut-off radii r_c . Because of the much smaller radius of the $1s$ orbital in Be, compared to He, the energetically appropriate cut-off radius r_c for the pseudo-interaction is substantially smaller. Also shown in Fig. 5 are the variational energies obtained for the Be ground state by removing the electron cusps [as defined in Eq. (C1)] from the accurate trial wave function which was determined by variance minimization for use in the DMC calculations. This trial wave function includes interelectronic terms and obtains 99.5% of the correlation energy. Removal of the cusp causes significant degradation of the quality of the wave function only for $r_c > 0.3$ atomic units, which is comparable to the typical separation of the $1s$ electrons. Thus, in Be, as in He, the success of interelectronic terms in obtaining good variational energies is not primarily due to their description of the short-range cusp behavior.

CI calculations using basis sets with s - and p -functions (the TZP basis of Ahlrichs *et al.*²⁸), s -, p -, and d -functions (6-311g*²⁹), s -, p -, d -, and f -functions (the ANO basis of Widmark *et al.*³⁰) and s -, p -, d -, f -, and g -functions (i.e., the ANO basis, augmented with a g -function with exponent 1.2) were carried out. The values of the CI coefficient threshold c_{\min} were taken to be 10^{-2} , 10^{-3} , and 10^{-4} for all basis sets. Calculations were carried out at cut-off radii r_c of 0 (i.e., Coulomb interaction), 0.1 and 0.2 a.u.

TABLE II. Calculated correlation energy, as a function of cut-off radius r_c and CI coefficient threshold c_{\min} , for the Be atom with the TZP basis set. All energies are in mHartree. The right-hand column shows the QMC correlation energy (i.e., the difference between the Hartree–Fock energy for this basis and the QMC energy) for each value of the cut-off radius r_c . The percentages indicated are the fractions of the QMC correlation energy for each value of r_c .

r_c (a.u.)	c_{\min}			HF – QMC
	1×10^{-2}	1×10^{-3}	1×10^{-4}	
0.20	51.63	60.91	61.61	99.39
	51.94%	61.28%	61.99%	100.00%
0.10	51.55	60.81	61.53	95.01
	54.26%	64.01%	64.76%	100.00%
0.00	56.42	61.51	62.01	94.89
	59.46%	64.82%	65.35%	100.00%

In Tables II and III we present the correlation energy for Be, obtained with the TZP and ANO basis sets, respectively. Figure 6 shows the number of CSF's as a function of the cut-off radius r_c for various values of the CI coefficient threshold c_{\min} in the MCCI approach. We see that, especially at the higher levels of accuracy (i.e., small c_{\min}), neither the fraction of the correlation energy obtained nor the number of CSF's used depend strongly on the cut-off radius r_c . As we saw in the He atom, removing the divergence of the Coulomb electron interaction does not substantially change the CI energy convergence at this level of accuracy.

IV. CONCLUSIONS

In this paper we have directly explored the effect of the electron cusp on the convergence of the energy for CI wave functions. To do so, we introduced a fictitious electron–electron interaction which, unlike the true Coulomb potential, does not diverge at electron coalescences and therefore has many-body eigenfunctions which are smooth there. The smooth potential is obtained by a method analogous to the well-established treatment of electron–ion interactions with smooth, norm-conserving pseudopotentials. These give scattering properties very similar to the true potential and improve the convergence of plane-wave expansions for single-particle wave functions. By analogy, one might expect that a similar treatment of the electron–electron interaction would improve the convergence of CI expansions.

For the He and Be atoms, we have compared the CI expansions of wave functions for the true, Coulomb interaction and for smooth pseudo-interactions between the electrons. We have also compared the variational energies of

TABLE III. Calculated correlation energy for the Be atom with the ANO basis set. The notation is the same as in Table II.

r_c (a.u.)	c_{\min}			HF–QMC
	1×10^{-2}	1×10^{-3}	1×10^{-4}	
0.20	53.40	71.35	74.13	90.39
	59.07%	78.93%	82.01%	100.00%
0.10	42.54	71.97	74.80	94.43
	45.05%	76.22%	79.21%	100.00%
0.00	58.46	72.30	74.66	93.91
	62.25%	76.99%	79.50%	100.00%

highly accurate wave functions containing r_{12} terms, where the cusp condition is exactly satisfied, with the energy for the same wave functions, from which the cusp has been deliberately removed out to a given radius.

The main result of our study is that a description of the electron cusp as such is *not* a limiting factor in calculating correlation effects with configuration interaction methods at the mHartree level of accuracy. We are led to this conclusion since the replacement of the divergent Coulomb interaction with a finite interaction leaves the convergence properties largely unchanged. The slow convergence of CI expansions in this energy range must be attributed to medium-range correlations, which are present for both types of electron interaction. The results obtained by explicitly removing the cusp from accurate variational wave functions support this conclusion, showing that the cusp of the wave function is not energetically important. This is found, even when cusplike behavior is removed out to a distance of half the typical interelectronic separation.

When describing correlation effects with explicit r_{12} methods, it is a mistaken notion to assign the improvement in convergence to their ability to describe the short-range cusp. Rather, the improvement in convergence at the mHartree level must be understood in terms of a better description of medium-range correlations when expressed in interelectronic coordinates. This fact must be considered when developing theoretical treatments of the electronic correlation problem.

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APPENDIX A: GENERATION OF ELECTRON PSEUDO-INTERACTIONS

The procedure for constructing the electron pseudo-interaction V_{ps} follows Hamann's construction¹⁹ of generalized norm-conserving pseudopotentials for electron–ion

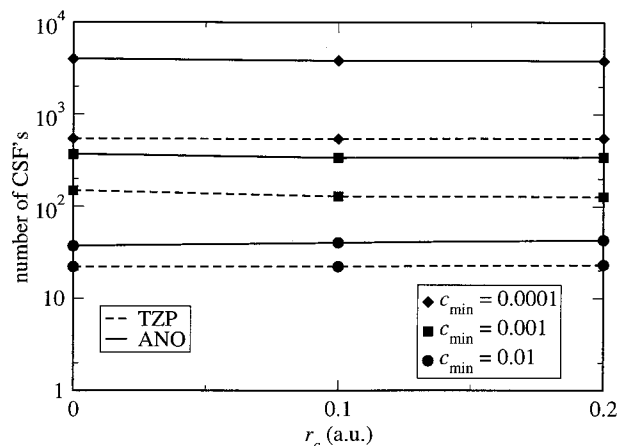


FIG. 6. The number of configuration state functions (CSF) in the CI expansion for the Be atom with TZP and ANO basis sets. Results are presented for coefficient thresholds c_{\min} of 0.01, 0.001, and 0.0001 at cut-off radii r_c of 0.0, 0.1, and 0.2 a.u.

scattering, with two modifications: (i) only two particles are involved in the generation of the electron–electron pseudo-interaction, so that we do not need to include screening potentials; (ii) because we are solving the scattering problem in the center-of-mass frame of the electrons and use the relative coordinate \mathbf{r} of the electrons, the mass of the electron is replaced by the reduced mass for the two-electron system. In Hartree atomic units, the interaction potential is $V(r)=1/r$ and the reduced mass is $1/2$. The radial Schrödinger equation for the relative motion of two electrons is then

$$-\frac{d^2u_l}{dr^2} + \left(\frac{l(l+1)}{r^2} + (V - \epsilon_l) \right) u_l = 0, \quad (\text{A1})$$

where $u_l(r)$ is r times the wave function in the relative coordinates, with angular momentum l and energy ϵ_l (the kinetic energy of the separated electrons in the center-of-mass frame).

In the generation of a pseudopotential, the true potential and pseudopotential become identical outside a suitably chosen cut-off radius r_c and are constructed to have identical scattering phase shifts and energy derivative of the phase shift at a reference energy ϵ_l . A smooth pseudo wave function $u_{\text{ps}}(r)$ is generated numerically to ensure “norm-conservation,” i.e., $u_{\text{ps}}(R_\infty) = u_l(R_\infty)$ and

$$\int_0^{R_\infty} u_{\text{ps}}(r)^2 dr = \int_0^{R_\infty} u_l(r)^2 dr, \quad (\text{A2})$$

for all $R_\infty \gg r_c$. In practice, we choose $R_\infty \sim 2.5r_c$, as in Ref. 19. Given u_{ps} , a smooth, finite pseudopotential V_{ps} is generated by inversion of the Schrödinger Eq. (A1) for $r < R_\infty$, with u_l and V substituted by u_{ps} and V_{ps} , respectively. We follow the steps exactly as given in Sec. II of Ref. 19, except where the reduced mass enters in the final inversion, slightly modifying Eq. (12) of Hamann’s work.

In the norm-conserving pseudopotential approach, different scattering potentials are often generated for different values of the angular momentum l . The full many-body wave function is anti-symmetric with respect to exchange of any two electrons. Thus, if the two electrons have parallel spin, the orbital part of the wave function must have odd parity and the allowed angular momentum l must be odd. Thus, the dominant parallel-spin scattering has $l=1$. For singlet (anti-parallel) scattering, the orbital part is symmetric and l must be even, with dominant allowed angular momentum $l=0$. Following the usual pseudopotential approach, we might then expect to generate a parallel-spin scattering potential using $l=1$ and an anti-parallel-spin scattering potential using $l=0$. In practice, we find that the $l=0$ potential gives good scattering for both angular momenta and the use of separate parallel- and anti-parallel-spin potentials is unnecessary.

Since ϵ_l is positive, the wave function will oscillate for large r , and if a node occurs for $r < R_\infty$, the inversion of the Schrödinger equation will fail. Thus, the joint requirements, that r_c be sufficiently large to produce a smooth pseudo-interaction and that $R_\infty \gtrsim 2.5r_c$, effectively limit the maximum reference energy ϵ_l at which the pseudo-interaction construction is possible.

We find that the pseudo-interaction is transferable (i.e., has very similar scattering strength to the true interaction) for energies over a wide range about the reference energy ϵ_l , as found previously for electron–ion pseudopotentials. In particular, we find that transferability is best for energies less than the reference energy at which the pseudopotential was generated. This would suggest that the best reference energy to use is the largest energy compatible with the procedure for inversion of the radial Schrödinger equation, a choice confirmed by calculations of many-body eigenstates using pseudo-interaction potentials generated with different values of the reference energy.

APPENDIX B: FIRST-ORDER PERTURBATION ANALYSIS OF PSEUDO-INTERACTIONS

In this Appendix, we consider the first-order error in the energy expected for a typical, arbitrary smooth electron–electron potential which is equal to the exact interaction $1/r$ outside some (adjustable) cut-off radius r_c . We will assume that the potential is (at least approximately) of the form

$$V_{r_c}(r) = \frac{1}{r_c} U(r/r_c), \quad (\text{B1})$$

where $U(r/r_c)$ is some universal function independent of r_c . Clearly both the true interaction $1/r$ and the smooth interaction V_{erf} are of this form exactly. V_{ps} is also approximately of this form. Thus, the difference ΔV between the interaction $V_{r_c}(r)$ and the true electron–electron interaction $1/r$ is of the same form

$$\Delta V(r) = \frac{1}{r_c} \Delta U(r/r_c), \quad (\text{B2})$$

where $\Delta U(\rho)$ is zero for $\rho > 1$.

Replacing the true electron–electron interaction with $V_{r_c}(r)$ then gives rise to a first-order energy error

$$\delta\epsilon^{(1)} = \langle \Psi | \Delta V | \Psi \rangle = \langle \Psi | \left(V_{r_c} - \frac{1}{r} \right) | \Psi \rangle, \quad (\text{B3})$$

where $|\Psi\rangle$ is the eigenstate of the many-electron system. If $P(r)$ is the electron pair distribution function (averaged at the pair separation distance r), the energy error may be rewritten as

$$\begin{aligned} \delta\epsilon^{(1)} &= \int_0^\infty P(r) \frac{1}{r_c} \Delta U(r/r_c) 4\pi r^2 dr \\ &= r_c^2 \int_0^1 P(r_c \rho) \Delta U(\rho) 4\pi \rho^2 d\rho. \end{aligned} \quad (\text{B4})$$

If r_c is sufficiently small and the pair-distribution function $P(r)$ does not tend to zero at $r=0$, then $P(r_c \rho)$ may be replaced by $P(0)$ in the integral and $\delta\epsilon^{(1)} \approx KP(0)r_c^2$ for small r_c , where K is a constant for the type of interaction, defined by

$$K \equiv \int_0^1 \Delta U(\rho) 4\pi \rho^2 d\rho. \quad (\text{B5})$$

The construction of V_{ps} ensures that the energy error is identically zero for the two-electron scattering at the reference energy, and therefore, $K=0$ for V_{ps} . However, for an arbitrary smooth interaction (such as V_{erf}), K will not be zero.

APPENDIX C: SHORT-RANGE CORRELATION TERM OBTAINED FROM NORM-CONSERVING POTENTIAL

In the generation of the norm-conserving potential discussed in Appendix A, we obtained a pseudo wave function $u_{ps}(r)$, which is a solution to the radial Schrödinger equation at the scattering energy ϵ_l for the pseudo-interaction, and the wave function $u_l(r)$, which is the corresponding solution for the true Coulomb interaction. The ratio $J_{sr} = u_l/u_{ps}$ of these two functions has the correct electron cusp (i.e., logarithmic derivative of $-1/4$ or $-1/2$ for parallel or anti-parallel spins, respectively, at $r=0$) and tends rapidly to 1 for $r > r_c$. This function J_{sr} may be said to contain the short-range cusp behavior of the Coulomb scattering solution, since it represents the difference between the scattering wave function for the divergent potential and that for the finite pseudo-interaction.

Moreover, if $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is a many-electron wave function (e.g., one which has inter-electronic coordinates r_{ij} explicitly included) with the correct electron cusps, the function

$$\Psi_s = \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \left/ \prod_{i < j} J_{sr}(r_{ij}) \right., \quad (\text{C1})$$

is smooth at electron coalescences but has very similar electron correlations for $r_{ij} > r_c$. The wave function Ψ_s has the electron cusp behavior of the original wave function Ψ removed inside the cut-off radius r_c , but is otherwise the same as Ψ . Thus, the energy difference $\langle \Psi_s | H | \Psi_s \rangle - \langle \Psi | H | \Psi \rangle$ is a good measure of the energy cost of removing the electron cusp behavior for $r < r_c$ from a correlated wave function, while keeping other aspects of the wave function (e.g., any benefits there may be to the inclusion of interelectronic coordinates in the form of the trial function) unchanged.

APPENDIX D: EVALUATION OF TWO-ELECTRON GAUSSIAN INTEGRALS WITH PSEUDO-INTERACTIONS

In this Appendix, we give details of the evaluation of two-electron Gaussian basis set integrals for the electron interactions, V_{erf} and V_{ps} , and their incorporation into existing electron integral programs.

For the interaction V_{erf} , the necessary modification of two-electron integrals for all s -type basis functions have been given by Savin.²⁰ We do not use Savin's approach, but rather directly modify the Rys quadrature approach of Dupuis, Rys, and King,²⁵ to obtain matrix elements for the interaction V_{erf} in place of those for $1/r_{12}$. To evaluate two-electron integrals for the pseudo-interaction V_{ps} , we use the form given in Eq. (3). This involves the evaluation of integrals with the interaction V_{erf} and a sum of Gaussian terms. In codes (e.g., the ARGOS code³¹) which use the Rys quadrature²⁵ approach for the evaluation of two-electron integrals with the Coulomb

interaction, these Gaussian terms are already evaluated in an intermediate stage and may be used in the present context.

Let us define two-electron integrals of the Coulomb interaction as

$$\left(\phi_i \phi_j \left| \frac{1}{r_{12}} \right| \phi_k \phi_l \right) \\ \equiv \int \int \phi_i(r_1) \phi_j(r_1) \frac{1}{r_{12}} \phi_k(r_2) \phi_l(r_2) dr_1 dr_2,$$

for Gaussian basis functions

$$\phi_i(r) = \exp(-a_i |r - R_i|^2) \prod_{x,y,z} (x - X_i)^{n_{xi}}.$$

The Rys scheme represents the $1/r_{12}$ term in Gaussian integral form, to obtain

$$\left(\phi_i \phi_j \left| \frac{1}{r_{12}} \right| \phi_k \phi_l \right) = \frac{2}{\sqrt{\pi}} \int_0^\infty du (\phi_i \phi_j | \exp(-u^2 r_{12}^2) | \phi_k \phi_l). \quad (\text{D1})$$

This integral is then transformed to an integral over the variable t , where $t^2 = u^2/(\rho + u^2)$ and $1/\rho = 1/(a_i + a_j) + 1/(a_k + a_l)$

$$\left(\phi_i \phi_j \left| \frac{1}{r_{12}} \right| \phi_k \phi_l \right) = \int_0^1 P_L(t) \exp(-X t^2) dt, \quad (\text{D2})$$

where P_L is a polynomial and $X = \rho |r_A - r_B|^2$. Here, r_A and r_B are the usual weighted-average centers of the Gaussian orbital pairs (i, j) and (k, l) , respectively, as given in Ref. 25. The integration over t is then evaluated exactly by an n -point quadrature formula

$$\left(\phi_i \phi_j \left| \frac{1}{r_{12}} \right| \phi_k \phi_l \right) = \sum_{\alpha=1}^n P_L(t_\alpha) W_\alpha,$$

where $t_\alpha(X)$ and $W_\alpha(X)$ are determined as in Ref. 25.

We observe that the interaction V_{erf} may be written in exactly the same form as in Eq. (D1), replacing the upper limit of integration ($u = \infty$) with $u = 1/r_c$. This changes the upper limit of integration in the variable t from 1 to $t_c = 1/\sqrt{1 + \rho r_c^2}$ in Eq. (D2). To use directly the Rys quadrature approach, we further transform to the variable $t' = t/t_c$, to obtain

$$\left(\phi_i \phi_j \left| \frac{\text{erf}(r_{12}/r_c)}{r_{12}} \right| \phi_k \phi_l \right) = t_c \int_0^1 P_L(t_c t') \exp(-X t_c^2 t'^2) dt',$$

which can be evaluated as

$$\left(\phi_i \phi_j \left| \frac{\text{erf}(r_{12}/r_c)}{r_{12}} \right| \phi_k \phi_l \right) = \sum_{\alpha=1}^n P_L(t'_\alpha) W'_\alpha,$$

where the quadrature points t'_α and weights W'_α are found by defining $X' = X t_c^2$, $t'_\alpha = t_c t_\alpha(X')$, and $W'_\alpha = t_c W_\alpha(X')$.

We can similarly evaluate the Gaussian terms in the representation of V_{ps} . Defining the integrand in Eq. (D1), $\mathcal{F}(u) \equiv (\phi_i \phi_j | \exp(-u^2 r_{12}^2) | \phi_k \phi_l)$, we see that $\sum P_L(t_\alpha) W_\alpha = \sum A_\alpha \mathcal{F}(u_\alpha)$, where $u_\alpha^2/\rho = t_\alpha'^2(1 - t_\alpha'^2)$ and $A_\alpha = (2/\sqrt{\pi}) \times [(\rho + u_\alpha^2)^{3/2}/\rho] \exp[X u_\alpha^2/(\rho + u_\alpha^2)] W_\alpha(X)$. One may directly

modify this finite-point quadrature summation to evaluate two-electron integrals for the Gaussian terms, replacing n with n_G , A_α with c_i , and u_α^2 with d_i . We have applied these modifications to the two-electron integrals within the ARGOS code, part of the COLUMBUS program package.³¹

- ¹B. Klahn and J. D. Morgan III, *J. Chem. Phys.* **81**, 410 (1984).
- ²R. N. Hill, *J. Chem. Phys.* **83**, 1173 (1985).
- ³J. D. Morgan, in *Numerical Determination of the Electronic Structure of Atoms, Diatomic, and Polyatomic Molecules*, edited by M. Defranceschi, and J. Delhalle (Kluwer Academic Publishers, Dordrecht, 1989), p. 49.
- ⁴W. Kutzelnigg and W. Klopper, *J. Chem. Phys.* **94**, 1985 (1991).
- ⁵W. Kutzelnigg and J. D. Morgan III, *J. Chem. Phys.* **96**, 4484 (1992).
- ⁶M. Hoffmann-Ostenhoff, T. Hoffman-Ostenhof, and H. Stremnitzer, *Phys. Rev. Lett.* **68**, 3857 (1992).
- ⁷T. Helgaker, W. Klopper, W. Koch, and J. Noga, *J. Chem. Phys.* **106**, 9639 (1997).
- ⁸T. Leininger, H. Stoll, H.-J. Werner, and A. Savin, *Chem. Phys. Lett.* **275**, 151 (1997).
- ⁹M. Nooijen and R. J. Bartlett, *J. Chem. Phys.* **109**, 8232 (1998).
- ¹⁰I. Silanes, J. M. Ugalde, and R. J. Boyd, *J. Mol. Struct.: THEOCHEM* **527**, 28 (2000).
- ¹¹T. Kato, *Commun. Pure Appl. Math.* **10**, 151 (1957).
- ¹²E. A. Hylleraas, *Z. Phys.* **51**, 347 (1929).
- ¹³R. Bukowski, B. Jeziorski, and K. Szalewicz, *J. Chem. Phys.* **100**, 1366 (1994).
- ¹⁴J. D. Baker, D. E. Freund, R. N. Hill, and J. D. Morgan III, *Phys. Rev. A* **41**, 1247 (1990).
- ¹⁵T. L. Gilbert, *Rev. Mod. Phys.* **35**, 491 (1963).
- ¹⁶H. F. King, *Theor. Chim. Acta* **94**, 345 (1996).
- ¹⁷D. R. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).
- ¹⁸W. E. Pickett, *Comput. Phys. Rep.* **9**, 115 (1989).
- ¹⁹D. R. Hamann, *Phys. Rev. B* **40**, 2980 (1989).
- ²⁰A. Savin, in *Recent Developments and Applications of Modern Density Functional Theory*, edited by J. M. Seminario (Elsevier, New York, 1996), p. 327.
- ²¹C. Filippi and C. J. Umrigar, *J. Chem. Phys.* **105**, 213 (1996).
- ²²C. J. Umrigar, K. G. Wilson, and J. W. Wilkins, *Phys. Rev. Lett.* **60**, 1719 (1987).
- ²³J. C. Greer, *J. Chem. Phys.* **103**, 1821 (1995).
- ²⁴J. C. Greer, *J. Comput. Phys.* **181**, 146 (1998).
- ²⁵M. Dupuis, J. Rys, and H. F. King, *J. Chem. Phys.* **65**, 111 (1976).
- ²⁶E. R. Davidson, S. A. Hagstrom, S. J. Chakraborty, V. M. Umar, and C. F. Fischer, *Phys. Rev. A* **44**, 7071 (1991).
- ²⁷T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- ²⁸A. Schaefer, H. Horn, and R. Ahlrichs, *J. Chem. Phys.* **97**, 2571 (1992).
- ²⁹R. Krishnan, S. J. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650 (1980).
- ³⁰P. O. Widmark, P. A. Malmqvist, and B. O. Roos, *Theor. Chim. Acta* **77**, 291 (1990).
- ³¹R. Shepard, I. Shavitt, R. M. Pitzer *et al.*, *Int. J. Quantum Chem., Symp.* **22**, 149 (1988).